

# *Atmospheric Deposition: PCBs, PAHs, Organochlorine Pesticides, and Heavy Metals*

## **Background**

Atmospheric deposition refers to substances that are deposited on land or water surfaces from the air. These substances can be carried in precipitation, also called wet deposition. They can also reach the earth's surface via dry deposition, which includes both the settling out of particles and the adsorption by soil, trees, water or other surfaces of gaseous substances.

An important category of atmospheric deposition is toxic pollutants including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), and heavy metals, including mercury. Although emissions and ambient concentrations of many of these substances have been estimated and measured elsewhere, there have been few studies that provided measurements or estimates of the amounts of these entering New Jersey's environment via atmospheric deposition. Now, with the recent completion of the New Jersey Atmospheric Deposition Network (NJADN) project,<sup>1</sup> sufficient data exist to establish baseline wet deposition quantities of these substances. NJADN also provided data on atmospheric concentrations of gaseous PCBs, PAHs and OCPs, and concentrations of these substances on particles in the atmosphere less than 2.5 micrometers in diameter (PM 2.5). These gas-phase and particle-phase concentrations can be used to estimate dry deposition quantities. Data provided through NJADN is still being reviewed and evaluated by the DEP. Preliminary findings are provided herein. More detail on NJADN will be available at the NJDEP Division of Science, Research & Technology website.<sup>2</sup>

## **Status**

The NJADN results, obtained at multiple sites in the State during the period from 1998 to 2001, establish baseline values for the air concentration and deposition in New Jersey of a number of important pollutants. Additional sampling and monitoring in the future will be necessary to determine any trends in these measurements. A summary of these baseline or status values for PCBs, PAHs, OCPs, and metals is provided on page 3.<sup>3</sup>

## PCBs

PCBs were manufactured and used in a variety of products before they were banned in the late 1970s. There are many different specific molecules, or congeners, that comprise the category known as PCBs. NJADN measured congeners that were found in the mixtures of PCBs that were produced and intentionally used. The concentrations of the measured PCBs are frequently summed and reported as total PCBs ( $\Sigma$  PCBs). NJADN measured concentrations of PCBs in air (gas phase), aerosol (particle phase) and precipitation at ten New Jersey sites representing a variety of land-use regimes at regular intervals from October 1997 through January 2003.

Gas-phase  $\Sigma$ PCB concentrations vary over more than two orders of magnitude from site to site in the region, with highest concentrations typically occurring in the urbanized areas of Camden and Jersey City, where concentrations averaged as high as 3600 picograms per cubic meter ( $\text{pgm}^3$ ) and 1250  $\text{pgm}^3$ , respectively. These concentrations were not high enough, however, to present significant health risk to humans due to inhalation. At most sites in the state, concentrations were in the 150 to 200  $\text{pgm}^3$  range, which is also similar to concentrations observed at sites surrounding the Great Lakes. Typically, less than 10% of the total atmospheric  $\Sigma$ PCB burden was found in the particle phase. PCBs in the particle phase generally followed the same spatial trends as the gas phase with Camden and Jersey City exhibiting the highest concentrations and several sites (Chester, Pinelands, Sandy Hook, Tuckerton, Washington Crossing, Alloway Creek) displaying concentrations that rarely exceed 40  $\text{pg m}^{-3}$ . The spatial distribution of particle-phase PCBs observed in New Jersey demonstrates that, like gas-phase PCBs, particle-phase PCBs in this region arise from sources that are highly localized in urban areas. Concentrations in precipitation at different sites also varied over two orders of magnitude. The spatial variations in concentrations mirrored those of the gas-phase, with highest concentrations occurring at Camden and Jersey City, followed by New Brunswick and Sandy Hook.

Based on the measured gas, particle, and precipitation phase concentrations, NJADN researchers estimated the atmospheric deposi-

tion flux, or flow, of  $\Sigma$ PCBs at the different sites. It was found that at most sites, the component of deposition that reflects the transfer of gas phase molecules to surfaces makes the largest contribution to overall deposition. The wet deposition component is relatively small at all sites.

It is important to note that these deposition estimates reflect the flow of PCBs from the atmosphere to the ground or to water surfaces, but they do not include estimates of the reverse flow. If a water body, for example, has a relatively large concentration of PCBs, some of this concentration will typically vaporize, i.e., move from the water to the air. This flow can be large enough in some cases to overwhelm the flow of PCBs from the air to the water, making for a net flow, or flux, from water to air. NJADN made estimates of the net flux of PCBs in the Hudson River Estuary, but did not make similar estimates for other water bodies due to lack of sufficient information on PCB concentrations in the waters themselves. In the case of the Hudson River Estuary, the atmospheric deposition of PCBs is small compared to other inputs, such as from known PCB contaminated locales in the Upper Hudson. Nevertheless, the atmospheric load of PCBs is large enough to be of concern there, and may well be a concern for other water bodies as well.

#### Polycyclic aromatic hydrocarbons (PAHs)

Atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in the gas and particle phases in air and in precipitation at nine New Jersey sites at regular intervals from October 1997 through May 2001. It was found that PAH concentrations vary spatially across the State of New Jersey with the highest concentrations occurring at the most heavily urban and industrial locations. Although the absolute concentrations vary spatially, the PAH profiles are statistically similar at nine of the ten sampling sites indicating that the mix of sources around New Jersey is the same. PAH concentrations measured in urban/industrial New Jersey (Jersey City and Camden) are reported by NJADN researchers to be of a similar magnitude to those measured in urban/industrial Baltimore, Maryland and over the southern basin of Lake Michigan adjacent to Chicago, Illinois and Gary, Indiana, two heavily urban and industrialized areas. No clear seasonal trend is apparent in the concentrations of any of the PAHs. PAH concentrations were also measured in rainfall. In rainfall, the concentrations were found to depend on the particular PAH molecules. Atmospheric deposition fluxes of PAHs were estimated based on measurements and models that are described in detail in the NJADN final report.

For most PAHs, gas absorption represents the single largest component of total atmospheric deposition for each of the sites, followed by dry particle deposition. Wet deposition constitutes the smallest fraction of the total atmospheric flux (3 to 16%). Annual average PAH total atmospheric deposition fluxes in New Jersey range from  $5.4 \times 10^2$  to  $7.3 \times 10^3$  ug/m<sup>2</sup> year. The order of highest to lowest fluxes follows the trend: Jersey City, Camden, Sandy Hook, Tuckerton, New Brunswick, Alloway Creek, Pinelands, and Chester.<sup>4</sup>

#### Organochlorine Pesticides

Organochlorine Pesticides (OCPs), including DDT and its metabolites, aldrin, dieldrin, heptachlor, endosulfan, chlordanes, and hexachlorohexane (HCH) were widely used in North America until the 70's when most were banned.

DDT was first used to control disease spreading insects and then as multipurpose insecticide. The peak of production of DDT in the U.S. was 82 million kg in 1962, and it was deregistered in 1972 except for public health emergencies. Aldrin and dieldrin were extensively used from the 1950s to the 1970s to fight insects on corn, cotton and citrus crops and also used as a termiticides. Aldrin is quickly metabolized to dieldrin in the environment. The peak usage of aldrin and dieldrin was in 1956 and both OC pesticides were banned in 1987 by the EPA.<sup>5</sup> Heptachlor was used during the 1960s and 1970s primarily by farmers to kill termites, ants, and soil insects in seed grains and on crops, as well as by exterminators and homeowners to kill termites. Phase out of heptachlor began in 1978. In 1988, the EPA canceled all uses of heptachlor in the U.S. The only commercial use still permitted is for fire ant control in power transformers. Heptachlor is still available outside the U.S.<sup>6</sup> Endosulfan is a chlorinated hydrocarbon insecticide and acaricide that acts as a poison to a wide variety of insects and mites on contact. It is still used in certain restricted ways. Chlordane was mostly used as an agricultural pesticide on corn and citrus, for home lawns and gardens and as termiticide in house foundations. Hexachlorohexane (HCH) was used as a mixture of several isomers until 1978, after which it was substituted by a purified isomer (lindane). Lindane has not been made in the United States since 1977 but it is still imported into the country. Its usage has been restricted by the U.S. EPA to certified individuals.

Many OCPs are still used in other parts of the world. These chemicals persist in the environment and biomagnify. Their presence at relatively high levels in the tissues of many animal species has been implicated in reproductive difficulties, for example, DDT has been shown to cause eggshell thinning and hatching failure of predator birds, including the Bald Eagle. Twenty years after they have been banned, OCPs are still ubiquitous in the environment.

Organochlorine Pesticides were measured in 2000-2001 at six locations in New Jersey as part of NJADN. It was found that higher air temperatures are associated with higher concentrations of most OCPs. Lower than expected concentrations were observed when the air mass came from the northwest (Canada and Great Lakes), whereas higher than expected concentrations showed no correlation with the air mass origin.

Gas phase concentrations comprise about the 95% of the measured quantities of OCPs across all samples in New Jersey.

Using estimation methods similar to those used for PCBs and PAHs, based on literature values for partition coefficients and related parameters, NJADN researchers estimated the atmospheric deposition flux for the measured OCPs. These values are shown in the table "OCP Atmospheric Deposition Fluxes" below.<sup>7</sup>

The NJADN data represent the first measurements of organochlorine pesticides in New Jersey air, and allowed the first estimates of atmospheric deposition of such pesticides to the New York-New Jersey Harbor Estuary. Although it is difficult to detect significant differences in deposition fluxes between any of the NJADN sites, it may be reasonably assumed that higher concentrations will lead to higher deposition fluxes. Atmospheric concentrations of dieldrin, aldrin, and the HCHs are similar to those measured in the Great Lakes region, suggesting that the New Jersey receives atmospheric deposition fluxes of these compounds that are similar to those received by the Great Lakes. In contrast, concentrations of DDTs, chlordanes, and heptachlor were higher in New Jersey than in the Great Lakes region.

Most of the pesticides measured through NJADN display their highest concentrations at Camden and New Brunswick, although in many cases the differences in mean concentrations are not statistically significant, and no clear correlation was found between urbanization and high atmospheric levels of OCPs. High atmospheric OCP levels are likely to be associated with past or present pesticide use (i.e. agricultural areas). High OCP levels at New Brunswick are therefore not surprising, as this site is located within Rutgers Gardens and less than a mile from the fields used by Rutgers and Cook College for decades of agricultural research. It is speculated that the high

**OCP Atmospheric Deposition Fluxes**  
**Units are ng m<sup>-2</sup> d<sup>-1</sup>. Blank spaces indicate**  
**the pesticide was not detected in that phase at that site**

	Gas Absorption						Dry Particle Deposition					Wet Deposition		
	CC	DB	JC	NB	PL	SH	CC	DB	JC	NB	PL	CC	JC	PL
alpha-HCH	42	8.1	11	43	26	9.7								
gamma-HCH	68	10	11	34	22	9.1								
sum HCHs	110	18	22	77	48	19								
Heptachlor	10	0.12	11	5.1	1.7	1.6								
Dieldrin	25	2.4	3.2	15	15	4.2			1.2					
Aldrin	7.4	0.00048	0.43	2.6	0.19	0.20			0.10					
Endosulfan I	33	4.1	5.4	80	22	6.3	0.87	0.36	0.42	0.22	0.39	0.46	0.14	0.46
Endosulfan II	NC	NC	NC	NC	NC	NC	1.8	1.0	0.70	0.90	0.94	2.4	0.88	0.85
Endosulfan sulfate							0.72	0.44	0.35	0.43	0.60	1.3	0.66	1.1
Oxychlordane							0.052			0.097	0.027	0.0095	0.010	0.025
Σ-Chlordanes	144	16	34	147	39	27	2.8	0.42	2.7	1.8	0.46	0.52	0.55	0.20
Σ-DDTs	31	2.1	8.7	62	8.0	14	1.5	0.71	2.1	1.2	0.25	0.57	1.1	0.17

NC = Not calculated.

CC = Camden, DB = Delaware Bay, JC = Jersey City, NB = New Brunswick, PL = Pinelands, SH = Sandy Hook

OCP levels observed in Camden may be due to its location downwind of rich agricultural areas in eastern Pennsylvania, not to its urban character. Also, DDT was once manufactured in the Philadelphia region.<sup>8</sup>

### Heavy Metals

Concentrations in precipitation and in small atmospheric particles (PM 2.5) of a number of inorganic chemicals, including a number of heavy metals, were measured as part of NJADN. These measurements permitted a calculation of the wet deposition of these substances, and an estimation of the dry deposition due to particle fall-out. These results are summarized in the tables "Deposition Fluxes of Inorganic Chemicals in NJ Precipitation" and "Dry Particle Deposition Fluxes of Inorganic Chemicals in NJ" below.<sup>9</sup>

Deposition of certain of the measured substances displayed attributes that are interesting and perhaps important, and could indicate pathways for future research.

Arsenic (As), cadmium (Cd), copper (Cu), and lead (Pb): These elements are emitted from a variety of industrial and municipal sources and, with the exception of As, were found to be strongly associated with particulate matter. The atmospheric concentrations and deposition of As, Cd, Cu, and Pb are generally lowest in the Pinelands and highest in Jersey City and Camden. Seasonal variations in the volume mean weighted concentrations in precipitation of As, Cd, and Cu were not uniform across New Jersey indicating the importance of local sources and/or atmospheric transport processes to the deposition of these trace elements in the state. In contrast, the seasonal

#### Deposition Fluxes of Inorganic Chemicals in NJ Precipitation

*Annual deposition fluxes ( $\mu\text{g m}^{-2} \text{ y}^{-1}$ )*

*BD = flux not calculated since all VWM concentrations were below the detection limit.*

*NA = not analyzed.*

<u>Element</u>	<u>New Brunswick</u>	<u>Jersey City</u>	<u>Pinelands</u>	<u>Camden</u>	<u>Alloway Creek</u>
Ag	25	21	59	38	BD
Al	35,000	28,000	24,000	56,000	34,000
As	67	160	65	150	130
Cd	62	76	23	71	39
Cl	340,000	750,000	220,000	560,000	NA
Co	46	130	22	160	30
Cr	150	180	56	310	65
Cu	1,500	2,200	490	2,000	790
Fe	47,000	47,000	23,000	87,000	38,000
Hg	11	14	11	14	5
Mg	65,000	81,000	54,000	84,000	89,000
Mn	2,500	1,900	2,900	3,400	2,700
Ni	650	1,200	290	980	270
NO <sub>3</sub> -N	360,000	360,000	390,000	420,000	310,000
PO <sub>4</sub> -P	7,100	5,200	8,300	8,100	NA
Pb	1,700	2,500	650	3,500	770
Pd	10	20	8.1	18	3.6
Sb	85	170	140	140	310
SO <sub>4</sub> -S	570,000	770,000	670,000	900,000	NA
V	580	880	410	1,100	430
Zn	7,800	8,800	5,500	12,000	10,000

variation in the concentrations of Pb was similar at all sites and showed the highest levels in the spring and the lowest levels in the fall or winter. The atmospheric deposition fluxes of Cd, Cu, and Pb illustrate the presence of an urban signal above the regional background that may indicate local sources. The wet deposition fluxes of Cd, Cu, and Pb at the urban/suburban NJADN sites (New Brunswick, Jersey City, Camden) are two to nine times higher than those measured in the early 1990's at rural sites in Maryland and Florida (Landing et al., 1995). This trend is similar for the dry particle fluxes of Cd, Cu, and Pb.<sup>11</sup>

**Mercury:** Mercury (Hg) is of environmental concern because of the enrichment and toxicity of monomethylmercury in aquatic biota, birds, mammals, and humans. New Jersey has taken a number of actions to reduce emissions of mercury in recent years. The main avenue of input of mercury to the State's environment is atmospheric deposition, and so the mechanisms, variability, and trends in this deposition need to be examined. Although national measurement programs exist,<sup>12</sup> prior to the NJADN, few data have been collected on deposition of mercury in New Jersey

**Dry Particle Deposition Fluxes of Inorganic Chemicals in NJ**  
**Fluxes ( $\mu\text{g m}^{-2} \text{ y}^{-1}$ ) were estimated from the concentrations of metals in fine aerosols (PM<sub>2.5</sub>)**  
**and a deposition velocity of 0.5 cm/s<sup>10</sup>**

Element	NB	JC	PL	CC	WC	TK	XQ	SH	DB	AC
Ag	33	130	13	32	5.7	4.6	7.0	5.9	5.0	14
Al	7,200	13,000	9,700	12,000	9,700	6,900	5,400	15,000	8,300	7,000
As	100	150	75	110	100	160	140	99	100	77
Cd	32	100	16	44	30	16	30	23	21	21
Co	160	84	55	66	28	21	28	35	29	250
Cr	12,000	960	4,100	3,900	750	300	1,600	430	480	20,000
Cu	2,200	2,700	1,200	1,300	4,600	1,100	240	640	310	1,000
Fe	66,000	38,000	28,000	40,000	17,000	12,000	12,000	21,000	8,300	97,000
Hg	1.2	1.8	0.8	2.5	1.0	0.9	2.2	1.2	1.2	2.0
Mg	4,100	6,400	13,000	8,800	5,700	5,100	1,600	12,000	5,600	2,900
Mn	1,700	700	580	800	380	240	310	560	210	2,500
Ni	10,000	2,000	3,400	2,900	1,700	570	1,100	880	370	16,000
Pb	1,100	4,200	460	900	1,100	520	430	830	350	480
Pd	8.8	4.0	10	14	2.8	4.1	3.4	3.3	3.7	14
Sb	130	840	64	210	96	64	53	110	45	52
V	440	1,600	310	820	400	560	230	1,000	420	498
Zn	3,600	5,500	2,600	5,300	3,400	3,500	4,300	5,200	3,600	2,600

CC = Camden, DB = Delaware Bay, JC = Jersey City, NB = New Brunswick, PL = Pinelands, SH = Sandy Hook, WC = Washington's Crossing, TK = Tuckerton, XQ = Chester, AC = Alloway Creek

Concentrations of mercury in precipitation measured through NJADN varied widely, but were generally in the range of 15 to 115 pM (3 to 23 ng/l). Concentrations in precipitation show a strong seasonal pattern, with the highest in summer and fall and the lowest in winter and spring. The same seasonal pattern has been observed elsewhere. The maximum differences in rain water Hg concentrations among four of the New Jersey sites (excluding Alloway Creek) were also greater in the summer and fall (35-40 pM) than in the winter and spring (20-28 pM). This would suggest that localized phenomena are responsible for much of the increase in Hg concentrations in New Jersey rain in the summer and fall. Localized phenomena may include greater emissions from local sources and/or higher Hg oxidation rates as a result of increased levels of atmospheric oxidants such as  $O_3$ .<sup>13</sup>

It must be noted that the mercury data collected through NJADN do not include gaseous forms of mercury. Gas phase forms of mercury include  $HgO$ ,  $HgCl_2$ ,  $HgBr_2$ , and  $Hg(NO_3)_2 \cdot H_2O$ . These forms, collectively called reactive gaseous mercury (RGM) or oxidized mercury, are present in the atmosphere and comprise a significant portion of anthropogenic mercury emissions. As reactive gases, RGM species are expected to have relatively high deposition velocities similar to gases such as  $HNO_3$ . Thus very low concentrations of RGM could account for significant Hg deposition. For example, given an RGM concentration of  $40 \text{ pg m}^{-3}$  (average concentration measured for Solomons, MD) and a deposition velocity of  $1 \text{ cm s}^{-1}$ , the estimated annual deposition of RGM ( $13 \text{ } \mu\text{g m}^{-2}/\text{y}$ ) is comparable to wet deposition fluxes measured across New Jersey ( $14\text{-}18 \text{ } \mu\text{g m}^{-2}/\text{y}$ ).<sup>14</sup>

## Outlook and Implications

Research is needed to improve understanding of dry deposition, including both particles and gaseous molecules, especially for mercury. The wet deposition fluxes of Hg in suburban New Brunswick and the rural Pinelands were lower than those recorded at the more urban/industrial Jersey City and Camden locations suggesting that in addition to the regional Hg signal, local phenomena are also important to the wet deposition of Hg in New Jersey. Lower Hg concentrations in rain measured at rural sites (DE, NY/VT, and PA) than at more developed locations in New Jersey, Maryland, and Florida suggest that differences in local sources, meteorology, and atmospheric chemistry affect the variability of Hg concentrations in east coast rain. The New Jersey wet deposition fluxes of Hg, together with the nearly synoptic NADP results for Pennsylvania, show something of a spatial gradient in Hg deposition with relatively low Hg

deposition rates at the central Pennsylvania sites (Cambria and Tioga counties), higher deposition rates in eastern Pennsylvania (Valley Forge), and the highest deposition fluxes in New Jersey. This west to east increase in Hg wet deposition could be the result of increasing Hg emissions, changes in atmospheric chemistry at this mid-Atlantic latitude, or both. A careful inventory of Hg emissions coupled with an assessment of the variation in atmospheric oxidant concentrations in this region could address this issue.<sup>15</sup>

Also, as noted above, NJADN measurements of mercury did not include reactive gaseous forms (RGM). Although there are significant uncertainties in estimating the contribution of RGM to total mercury deposition, it is likely that this contribution is significant. The ambient concentrations, formation, and seasonal cycle of RGM in New Jersey need to be studied in order to assess the full impact of the atmospheric deposition of Hg in the State. Research on mercury should also include efforts to better understand the transport and fate mechanisms of mercury in the atmosphere, especially those that mediate its oxidation from elemental forms to reactive forms.

More information is necessary on PCBs. Their concentrations continue to be high enough in the Delaware Estuary and NY/NJ Harbor to be problematic, and numerous fish advisories for PCBs continue to be necessary. Local transport modeling and source apportionment studies should be supported and used to identify the major emissions sources of PCBs to the atmosphere. Included in this work should be investigation of possible fresh sources of PCBs to the environment from ongoing industrial processes (as opposed to emissions from legacy PCBs), including some congeners not investigated through NJADN.

The NJADN work also identified other issues associated with atmospheric deposition of toxics and other substances. Included is the need to better quantify and identify organic nitrogen deposition, and its sources. Also, assessments of the concentrations and deposition fluxes of emerging atmospheric contaminants such as brominated compounds are needed in the Mid-Atlantic region. In addition, studies focused on the evaluation of the watershed retention and runoff and ecosystem impacts of atmospheric contaminants are needed to evaluate the real impacts of atmospheric deposition as a major non-point source of contaminants to surface waters.

### ***More Information***

See the full NJADN report and summary material which will be available at the NJDEP Division of Science, Research & Technology web site, at <http://www.state.nj.us/dep/dsr/index.html>.

### ***References***

- <sup>1</sup> Reinfelder, John, Lisa Totten, and Steven Eisenreich, 2004, The New Jersey Atmospheric Deposition Network, Final Report to the NJDEP, Michael Aucott, project manager, NJDEP Division of Science, Research, & Technology, May, 2004 (NJADN Final Report)
- <sup>2</sup> <http://www.state.nj.us/dep/dsr/index.html>
- <sup>3</sup> See the separate chapter on PM<sub>2.5</sub> in this Environmental Trends series for a summary of NJADN findings regarding organic carbon and elemental carbon.
- <sup>4</sup> NJADN Final Report and references therein, p. 72
- <sup>5</sup> NJADN Final Report and references therein, p. 88
- <sup>6</sup> NJADN Final Report and references therein, p. 86
- <sup>7</sup> NJADN Final Report and references therein, p. 85
- <sup>8</sup> NJADN Final Report and references therein, pp. 96-97
- <sup>9</sup> NJADN Final Report and references therein, pages 123 & 125
- <sup>10</sup> The chosen deposition velocity was selected to capture the deposition of all size classes of atmospheric particles, but may underestimate the flux of elements primarily associated with large particles and over estimate the deposition of elements primarily associated with small particles. See NJADN Final Report and references therein, section I.C1, pp 13-14.
- <sup>11</sup> NJADN Final Report and references therein, pp. 127-130
- <sup>12</sup> See the National Atmospheric Deposition Program Mercury Deposition Network site at <http://nadp.sws.uiuc.edu/mdn>
- <sup>13</sup> NJADN Final Report and references therein, pp. 135-138
- <sup>14</sup> NJADN Final Report and references therein, p. 141
- <sup>15</sup> NJADN Final Report and references therein, p. 138-139